The Law of Distribution of Particles in Colloidal Solution.

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I. *Introduction.*

The work of Perrin and his collaborators (1) on the experimental and theoretical application of the results of the kinetic theory to colloidal solutions is probably the most complete exposition of this very interesting phase of modern work. In the course of the work, Perrin (2) shows that we should expect a law of distribution of the particles in a colloidal suspension analogous to that regulating the distribution of the molecules of air in the atmosphere.

By balancing the osmotic pressure of the particles in solution against the effect of gravity, he deduces the equation

$$\frac{RT}{N}\log\frac{n}{n_0} = V(\rho_1-\rho_2)g(h-h_0), \tag{1}$$

where n and n_0 are the numbers of particles per cubic centimetre, at depths h and h_0 from the top of the solution,

V is the volume of each particle,

ρ_1 and ρ_2, the densities of the material of the particles and the medium respectively,

and R, T, N, and g the ordinary constants.

Perrin tests the reliability of this equation by observations from which he quotes two typical series:—

1. For gamboge particles $2{\cdot}12\times10^{-5}$ cm. in diameter, the number of particles at four different depths differing successively by 3×10^{-3} ($30\,\mu$) were found to be proportional to the numbers

$$12 : 22{\cdot}6 : 47 : 100$$

which numbers are almost the same as the geometrical progression

$$11{\cdot}1 : 23 : 48 : 100.$$

2. For gamboge particles $5{\cdot}2\times10^{-5}$ cm. in diameter, similar observations of depths differing by 6×10^{-4} cm. ($6\,\mu$) gave numbers proportional to

$$305 : 530 : 940 : 1880$$

approximately given by

$$280 : 528 : 995 : 1880$$

which are in geometrical progression.

If the above equation be written

$$\log \frac{n}{n_0} = \mathrm{P}(h-h_0) \text{ where } \mathrm{P} = \frac{\mathrm{N}}{\mathrm{RT}} \cdot \mathrm{V} \cdot (\rho_1-\rho_2) \cdot g, \tag{2}$$

the two series of results give values for P as follows:

$$\text{I} \quad \mathrm{P}_1 = 100, \qquad \text{II} \quad \mathrm{P}_2 = 500.$$

As pointed out by Perrin, the concentration at a distance $9{\cdot}6 \times 10^{-3}$ cm. from the bottom of the dish would only be 1/60,000 of that at the bottom, and he adds, "hence, when permanent equilibrium has been reached, grains will hardly ever be found in the higher layers of such preparations."

Using the value of P as obtained above, we can easily find by calculation that the increase in concentration down a tube of a few centimetres depth would be an enormous multiple of the concentration at the top.

Perrin's experiments were carried out on gamboge particles, which were very large compared with the particles of ordinary colloidal solutions, and observations were confined to samples of these gamboge suspensions of very small depth. "Successful observations with the emulsions I have used cannot be made through heights of several centimetres or even millimetres; heights of less than a tenth of a millimetre only are suitable" (3).

Whether so intended by Perrin or not, this formula has been taken to hold for all colloidal solutions and for all depths. A little consideration will contradict the possibility of such an extension of Perrin's work.

For example, in a silver colloidal solution worked with by one of us (4), the value of P in the above formula would be given by substituting as follows in (2):—

$$\frac{\mathrm{RT}}{\mathrm{N}} = \text{(approx.) } 4 \times 10^{-14}, \qquad \rho_1-\rho_2 = 9{\cdot}5,$$

$$\mathrm{V} = 22 \times 10^{-15}, \qquad g = 980,$$

from which

$$\mathrm{P} = \text{(approx.) } 5000.$$

The ratio of the concentrations at any two levels 1 cm. apart would be given by the equation

$$\log \frac{n_1}{n_2} = 5000,$$

which is a result quite out of all reason, to one familiar with such solutions.

II. *Experimental Work.*

If there is any remarkable variation in the distribution of the particles in an ordinary colloidal solution, it should be shown by allowing the solution to stand in a long vertical tube for some time.

A glass tube, 3 cm. in diameter and 94 cm. in length, has small bent glass tubes sealed on at intervals along its length and closed at the ends. This long tube, after having been carefully cleaned with distilled water, was filled with copper colloidal solution of conductivity $4 \cdot 6 \times 10^{-6}$ and allowed to stand undisturbed for about fifty days in a room in which the temperature varied but little. The liquid in the different layers was then drawn off by means of the small tubes *a*, *b*, *c*, *d*, *e*, and *f*, and, after the conductivity was again measured, the liquid was evaporated and the residue weighed.

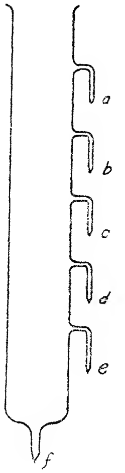

Fig. 1.

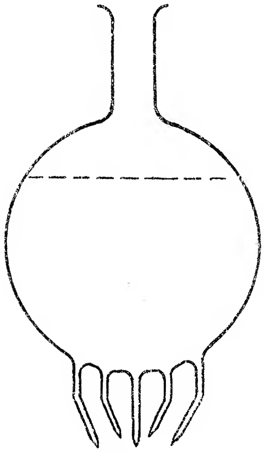

Fig. 2.

The results are tabulated below:—

Table I.

Number of layer.	Average depth from surface.	Conductivity of sample drawn off (20° C.).	Weight of copper in grm. per litre.
	cm.		
I	16·8	$7 \cdot 51 \times 10^{-6}$	0·0142
II	32·0	—	0·0138
III	47·8	$6 \cdot 88 \times 10^{-6}$	0·0152
IV	63·5	$6 \cdot 83 \times 10^{-6}$	0·0142
V	78·3	$6 \cdot 86 \times 10^{-6}$	0·0142
VI	93·3	$7 \cdot 41 \times 10^{-6}$	0·0166

A slight sediment in the bottom layer accounts probably for its increased weight and conductivity. For the rest, the weight is constant within the limits of experimental error. Evidently, even if Perrin's Law holds over a small depth, a limiting concentration is soon reached, so that no difference in density is shown for considerable depths.

A similar experiment was performed, using instead of the long tube a round litre flask with five small tubes sealed in the bottom (fig. 2). This was filled with copper colloidal solution of concentration 0·242 grm. per litre and conductivity $6·86 \times 10^{-6}$ at 20° C.

After standing about fifty days, the points of the five tubes were broken and the solution drawn slowly off into four dishes, inserted one after another. In this experiment the liquid was drawn off in layers as before, but they were less in depth and greater in area than in the previous case.

The concentrations determined were as follows:—

Table II.

Layer.	Concentration of copper in grms./litre.
I (top)	0·263
II	0·253
III	0·232
IV	0·235

This form of tube was not so well adapted to the purpose as the other, but, as before, the densities are practically constant.

To one familiar with colloidal solutions these experimental observations would have been foretold, but it remains to reconcile these results with those of Perrin on gamboge. That the concentration in such solutions tends to become uniform and is regulated by some definite properties of the particles is shown also by some experiments carried out by one of us and published some years ago (5). (See also Bancroft) (6).

"In connection with the influence of the medium the possibility of a limiting concentration is important.

"In his first paper on electrically prepared colloidal solutions, Bredig reports sols of the following concentrations:—

Platinum	20 mgrm. per 100 c.c.
Gold	14 mgrm. per 100 c.c.
Iridium	7 mgrm. per 100 c.c.

With the many platinum, gold, silver and copper solutions which the writer has prepared during the last few years the amount of metal per 100 c.c. has invariably been in the neighbourhood of 10 mgrm.

"The uniformity of these results points to some cause limiting the amount of metal which a given liquid will retain in the colloidal state. In order to find whether such solutions have a limiting concentration, 800 c.c. of silver hydrosol was prepared and gradually evaporated. At the beginning and at each successive stage at which the volume of the liquid evaporated reached a half value, the amount of metal per cubic centimetre, the mobility of the particles, and the size of the particles were determined; the results of these observations are recorded in Table III:—

Table III.

Concentrated to	Weight of Ag per 100 c.c.	No. of particles per c.c.	Volume of a single particle.	Mobility constant $V \times 10^{-5}$.
	mgrm.			
Original vol.	6·2	$2 \cdot 9 \times 10^8$	$2 \cdot 0 \times 10^{-14}$	25·2
0·5 original vol. ...	8·8	$4 \cdot 2 \times 10^8$	$2 \cdot 0 \times 10^{-14}$	23·5
0·25 „ „ ...	10·2	—	—	23·1
0·15 „ „ ...	12·3	—	—	—

"It will be seen that the size of the particles and their mobility is apparently not affected by the concentration of the solution. The variation in the amount of metal per 100 c.c. as the water was extracted from the sol is illustrated in the curve in fig. 3, in which the amount of metal per 100 c.c. at any time is plotted against the concentration if all the metal had remained in suspension. This indicates strongly that there is a limit to the quantity of colloidal silver possible in water, at about 13 mgrm. per 100 c.c.

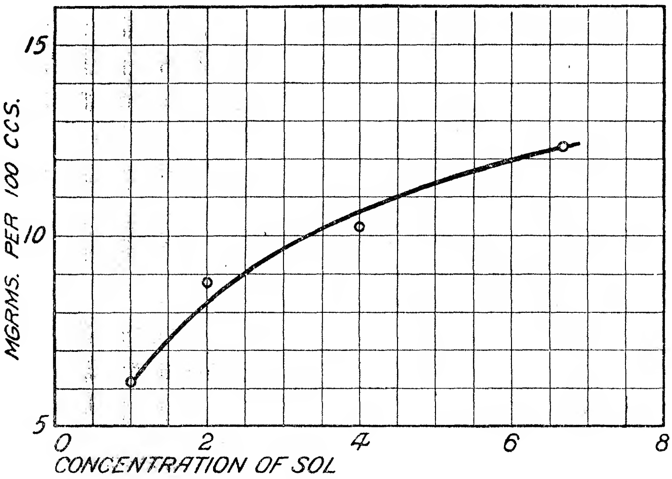

Fig. 3.

"In order to obviate any irregularity that might be introduced by heating the solution, the evaporation was carried on over sulphuric acid and calcium chloride at very low pressure, an operation extending over about a week.

" As this particular solution had been standing undisturbed and unchanged for a month before the evaporation was begun, the apparent settling of the metal is not due merely to the lapse of time. Again, it cannot be due to the concentration of electrolytic impurities in the sol, because these were not sufficient to have any appreciable effect, as is shown by the mobility determination for the first three samples." (5)

The only conclusion that can be drawn from these experiments is that fundametally these suspensions of fine particles always reach a uniform distribution throughout the body of the liquid, and the variation expressed in Perrin's distribution law must be confined to a very small distance at the surface.

REFERENCES.

(1) Perrin, 'Atoms,' tr. by Hammick (Constable, 1916).

(2) *Loc. cit.*, p. 90 *et seq.*

(3) *Loc. cit.*, p. 99.

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(5) Burton, "On the Physical Aspect of Colloidal Solutions," 'University of Toronto Studies,' No. 36, p. 48 (1910).

(6) Bancroft, 'Jour. of Phys. Chem.,' vol. 18, p. 558 (1914).

A New Form of Interferometer.

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The Lummer and Gehrke interferometer consists of a thin plate of glass with its two surfaces worked optically true and paralled to one another. High accuracy is required in the plane parallelism, and the flatness of surface and the difficulty of working such long plates for high resolving powers, and the cost involved, sets a limit to our achievement in this direction. Such plates, even when finished, furnish results which have given rise to a considerable amount of discussion and raise doubt as to whether the appearances are trustworthy at such high resolving powers and whether they are not partly due to ghosts formed by the defects in the glass. Hence the present attempt to devise a parallel plate that would meet these objections and serve as an instrument of resolving power and precision sufficient to extend our